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EP 0 488 353 B1

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Description**Field of the Invention**

- 5 The present invention relates to a method for corrosion-prevention treatment of metal surfaces.

Background of the Invention

There are known several methods for corrosion-prevention treatment of metal surfaces. A well-known 10 method comprises coating a metal surface with zinc by hot dip plating or electroplating followed by chromating. Another one is blast zinc plating. There has further recently been developed a new coating method which consists of projecting a shot material onto the surface of iron or an iron alloy, said shot material comprising an aggregate of particles each consisting of a core of iron or an iron alloy and an undercoat of an iron-zinc alloy and a top coat of zinc or a zinc alloy. (See Japanese Patent Publication No. 15 59-9312.) This method is referred to as the improved blast zinc coating method in this specification.

This method has several advantages including low equipment cost, less energy consumption, and least environmental pollution. However, this method does not provide a zinc coating having sufficient corrosion resistance. For example, a zinc coating with a coating weight of 100 mg/dm² permits red rust formation within 24 hours in the salt spray test. Presumably, this is due to the fact that the coating formed by this 20 method is an iron-zinc alloy.

Generally speaking, high corrosion resistance is not achieved by the conventional metal surface treatments such as zinc plating method, zinc-alloy plating method and the improved blast zinc coating method. In the case where high corrosion resistance is required, therefore, the treated object must be subjected to an aftertreatment.

25 A comparatively simple method of aftertreatment is chromating. If adequate chromating is effected after the improved blast zinc coating, neither red rust nor white rust form within 240-1000 hours. (See Japanese Laid open Patent Publication Nos.61-67773 and 2-19477.) Therefore, it is considered that employment of chromating as an aftertreatment is essential when the improved blast zinc coating method is applied to a metal surface for corrosion prevention.

30 A disadvantage of chromating as an aftertreatment is that a solution-containing a hexavalent chromium compound has to be used, which is detrimental from the viewpoint of safety and hygiene and a cause of environmental pollution. Hexavalent chromium compounds have to be handled with great care when used industrially.

35 US-A-4,341,558 describes a composition imparting corrosion resistance to metal surfaces containing a water soluble titanium zirconium compound, an inositol-2-6-phosphate ester and silica. Such a composition is applied to the metal surface and is dried in place, thus effluent problems occurring in conventional processes involving rinsing are avoided.

Although considerable research has been conducted in search of an aftertreatment that provides excellent corrosion resistance, no method has been developed that surpasses chromating treatment.

40 In search of a satisfactory aftertreatment for the improved blast zinc plating, we conducted intensive studies. As a result, we found a new aftertreatment method which is comparable to chromating treatment in corrosion prevention effect. Specifically, it was discovered that it is possible to produce the same effect as chromating by treating a metallic material to which the improved blast zinc coating has been applied with an aqueous suspension of silica and an aqueous solution containing ions of at least one metal selected from 45 Ti, Zr, Mg, Ba, Sr, W, Ni, Co, Sn, Mo, and Mn.

Summary of the Invention

The present invention provides a method for treating a metal surface which comprises projecting onto a 50 metal surface a shot-blast particulate material consisting of a core of iron or an iron alloy, an undercoat of an iron-zinc alloy and a top coat of zinc or a zinc alloy, thereby forming a coating film of zinc or the zinc alloy on the metal surface. Which method is characterized in that the thus coated metal surface is sequentially brought into contact with

- an aqueous suspension consisting of 0.1-20 parts by weight of silica per 100 parts by weight of water 55 and
- an aqueous solution consisting of 100 parts per weight of water and of at least one water soluble metal salt of at least one metal selected among Ti, Zr, Mg, Ba, Sr, W, Ni, Co, Sn, Mo and Mn, expressed in terms of 0,01-20 parts by weight of metal ions.

The first step of the present invention is the method disclosed in Japanese Patent Publication No. 59-9312 but it includes improvements thereof.

5 The silica used in the present invention may be either precipitated silica or vapor-phase-hydrolyzed silica. Any silica will do insofar as it forms an aqueous suspension. The aqueous suspension contains 0.1-20 parts by weight of silica per 100 parts by weight of water. With an amount of less than 0.1 part by weight, the silica does not form a satisfactory corrosion prevention film on the surface of the treated object. With an amount in excess of 20 parts by weight, the silica forms an undesirable thick gelled film on the surface of the treated object.

10 When the object is treated sequentially, i.e. with a neat silica suspension, the suspension is preferably kept at 5-40°C. With a temperature lower than 5°C, an unpractically long time is required for drying after the treatment. With a temperature higher than 40°C, the suspension is liable to cause early gelation of silica.

15 The object for treatment should be immersed in the aqueous suspension of silica for 10-25 seconds. Immersion for less than 10 seconds is too short for the suspension to form a perfect film on the surface of the object. Immersion for longer than 250 seconds is not practical.

20 The aqueous solution contains ions of one or more metals selected from among Ti, Zr, Mg, Ba, Sr, W, Ni, Co, Sn, Mo, and Mn.

These metal ions may be of any water-soluble metal salt. There is no restriction on pH of the aqueous solution. Any solution may be used insofar as it is aqueous.

25 The aqueous solution should contain 0.01-20 parts by weight of ions per 100 parts by weight of water. With an amount of less than 0.01 part of ions, an unduly long time is required for treatment because the reaction is slow. With an amount in excess of 20 parts by weight, sludge is formed on the surface of the treated object.

30 Treatment with the aqueous solution should be conducted at a temperature between 5°C and the boiling point. With a temperature lower than 5°C an unpractically long time is required for drying after the treatment.

The object to be treated should be immersed in the aqueous solution for 3-250 seconds. Immersion for shorter than 3 seconds or longer than 250 seconds is not practical for the treatment.

35 According to the present invention, after the object to be treated has been subjected to the improved blast zinc coating, it is dipped in the aqueous suspension of silica and the aqueous solution of metal ions.

The treatment with the aqueous suspension of silica and the treatment with the aqueous solution containing metal ions can also be conducted simultaneously by using a single medium containing the two materials. In this case, the treating liquid should be at 5-40°C. Here again, with a temperature lower than 5°C, an unpractically long time is required for drying after the treatment. With a temperature higher than 40°C, the treating liquid is liable to cause early gelation of silica.

40 The adequate immersion time ranges from 10 to 250 seconds. With an immersion time shorter than 10 seconds, the treating liquid does not form a perfect film on the surface of the treated object. Immersion longer than 250 seconds is not practical for the treatment.

45 The treatment may be accomplished by dipping, brushing, or spraying, with dipping being most practical.

The method of the present invention, in which the improved blast zinc coating is combined with the wet surface treatment, is as effective as the chromating treatment, and yet it does not cause environmental pollution unlike the chromating treatment.

It is assumed that the effect of the present invention is brought about by the fact that silica adsorbed on the zinc coating film seals the pores thereof and subsequently forms an amorphous coating film by combination with the metal ions.

Specific Disclosure of the Invention

50 The invention will be described in detail by way of working examples and comparative examples, which do not restrict the scope of the invention.

55 For testing, 100 x 5 x 20 mm mild steel test panels were used. The panels were degreased with trichloroethane vapor and, thereafter, coated with a zinc-iron alloy by the improved blast zinc coating method as disclosed in Japanese Patent Publication No. 59-9312. The thus treated test pieces were then subjected to the aftertreatment as described in the following Examples and Comparative Examples. The resulting test pieces were subjected to salt spray test as stipulated in JIS Z-23711. The corrosion resistance of the test pieces were rated by the time until white rust formed.

For comparison, the aftertreatment was also carried out on a mild steel test piece measuring 100 x 50 x 2.0 mm, which had been coated with (8 µm thick) zinc by electroplating. In the following examples, "parts" means "parts by weight".

5 Example 1

An aqueous treating suspension was prepared by uniformly dispersing 0.5 part of silica in 100 parts of deionized water with stirring. An aqueous treating solution was prepared by dissolving 0.5 part of K_2ZrF_6 (in terms of Zr ions) in 100 parts of deionized water. The test piece, which had been subjected to the improved blast zinc coating, was immersed in the aqueous suspension for 30 seconds, followed by drying with warm air. Thereafter, it was immersed in the aqueous solution for 60 seconds at room temperature, followed by drying with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

15 Example 2

The test piece was coated by brushing with the aqueous suspension of silica prepared in Example 1, followed by drying with warm air. The test piece was further coated by brushing with the aqueous solution containing K_2ZrF_6 prepared in Example 1, followed by drying with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

Example 3

In 100 parts of deionized water was suspended 5 parts of silica and further 1 part of $Ni(SO_3)_2 \cdot 4H_2O$ (in terms of Ni ions) was dissolved therein with stirring. The test piece, which had been subjected to the improved blast zinc coating, was immersed in the thus prepared treating liquid for 60 seconds, followed by drying with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

30 Example 4

The test piece was coated by brushing with the treating liquid containing silica and $Ni(SO_3)_2 \cdot 4H_2O$ prepared in Example 3, followed by drying with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

35 Example 5

In 100 parts of deionized water was suspended 10 parts of silica and also 1 part of $MnCl_2 \cdot 4H_2O$ (in terms of Mn ions) was dissolved therein with stirring. The test piece, which had been subjected to the improved blast zinc coating, was immersed in the thus prepared treating liquid for 60 seconds, followed by drying with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

Example 6

45 The test piece was coated by brushing with the treating liquid containing silica and $MnCl_2 \cdot H_2O$ prepared in Example 5, followed by drying with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

50 Example 7

An aqueous treating suspension was prepared by uniformly dispersing 5 parts of silica in 100 parts of deionized water with stirring. An aqueous treating solution was prepared by dissolving 0.5 part of K_2ZrF_6 (in terms of Zr ions) and 5 parts of $CoSO_4 \cdot 8H_2O$ (in terms of Co ions) in 100 parts of deionized water. The test piece (which had been subjected to the improved blast zinc coating, was immersed in the aqueous suspension for 30 seconds, followed by drying with warm air, and then in the aqueous solution for 60 seconds at room temperature, followed by drying with warm air. The treated test piece was tested for corrosion resistance test. The results are shown in Table 1.

Example 8

- The test piece was coated by brushing with the aqueous suspension of silica prepared in Example 7, followed by drying with warm air. The test piece was further coated by brushing with the aqueous solution containing K_2ZrF_6 and $CoSO_4 \cdot 8H_2O$ prepared in Example 7, followed by drying with warm air. The treated test piece was tested for corrosion resistance test. The results are shown in Table 1.

Example 9

- An aqueous treating suspension was prepared by uniformly dispersing 15 parts of silica into 100 parts of deionized water with stirring. An aqueous treating solution was prepared by dissolving 0.5 part of K_2TiF_6 (in terms of Ti ions) in 100 parts of deionized water. The test piece, which had been subjected to the improved blast zinc coating, was dipped in the aqueous suspension for 30 seconds, followed by drying with warm air, and then in the aqueous solution for 60 seconds at room temperature, followed by drying with warm air. The treated test piece was tested for corrosion resistance test. The results are shown in Table 1.

Example 10

- An aqueous treating suspension was prepared by uniformly dispersing 15 parts of silica in 100 parts of deionized water with stirring. An aqueous treating solution was prepared by dissolving 0.5 part of $MgSO_4 \cdot H_2O$ (in terms of Mg ions), 0.5 part of $(NH_4)_6Mo_7O_{24}$ (in terms of Mo), and 0.7 part of $SrCl_2 \cdot 6H_2O$ (in terms of Sr ions) in 100 parts of deionized water. The test piece, which had been subjected to the improved blast zinc coating, was immersed in the aqueous suspension for 30 seconds, followed by drying with warm air, and then immersed in the aqueous solution for 60 seconds at room temperature, followed by drying with warm air. The treated test piece was tested for corrosion resistance test. The results are shown in Table 1.

Example 11

- An aqueous treating suspension was prepared by uniformly dispersing 20 parts of silica in 100 parts of deionized water with stirring. An aqueous treating solution was prepared by dissolving 0.5 part of $SnCl_2$ (in terms of Sn ions) and 3 parts of $CoSO_4 \cdot 8H_2O$ (in terms of Co ions) in 100 parts of deionized water. The test piece (which had been subjected to the improved blast zinc coating) was immersed in the aqueous suspension for 30 seconds, followed by drying with warm air, and then immersed in the aqueous solution for 60 seconds at room temperature, followed by drying with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

Comparative Example 1

- A treating solution was prepared by uniformly dissolving 1.0 part of chromic anhydride, 0.1 part of sulfuric acid, and 0.1 part of nitric acid in 100 parts of deionized water. The test piece, which had been subjected to the improved blast zinc coating) was immersed in the treating solution for 4 seconds, and then allowed to stand in air, washed with water, and dried with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

Comparative Example 2

- A treating solution was prepared by uniformly dissolving 2.0 parts of chromic anhydride and 0.1 part of chromium nitrate in 100 parts of deionized water. The test piece which had been subjected to the improved blast zinc coating, was immersed in the treating solution for 4 seconds, and then allowed to stand in the air, washed with water, and dried with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

Comparative Example 3

- A treating solution was prepared by uniformly dissolving 15 parts of t-butanol, 2 parts of chromic anhydride, and 0.01 part of oxalic acid in 100 parts of trichlorofluoroethane. This solution was boiled under refluxing. The test piece which had been subjected to the improved blast zinc coating, was immersed in this

solution for 60 seconds, followed by forced drying at 40 °C for 3 minutes in fresh air. The treated test piece was washed with a mixed solvent of trichlorofluoroethane and t-butanol, followed by drying. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

5 Comparative Example 4

A treating solution was prepared by uniformly dissolving 1.0 part of tannic acid in 100 parts of deionized water. The test piece which had been subjected to the improved blast zinc coating, was immersed in the treating solution at 70 °C for 4 seconds, and allowed to stand in air, washed with water, and dried with warm air. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

Comparative Example 5

15 The test piece, which had been subjected to the improved blast zinc coating, was tested for corrosion resistance without chemical conversion being employed. The results are shown in Table 1.

Comparative Example 6

20 The test piece, which had been coated with zinc by electroplating instead of the improved blast zinc coating, was treated with the treating liquid used in Example 1. The treated test piece was tested for corrosion resistance. The results are shown in Table 1.

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Table 1

Example No.	Pretreatment	Chromium compound	Metal ion	Treating method	Salt spray Test
1	Blast coating	-	Zr 0.5 part	Dipping	550 hours
2	"	-	Zr 0.5 part	Brushing	450 hours
3	"	-	Ni 1.0 part	Dipping	1200 hours
4	"	-	Ni 1.0 part	Brushing	980 hours
5	"	-	Mn 1.0 part	Dipping	450 hours
6	"	-	Mn 1.0 part	Spraying	390 hours
7	"	-	Zr 0.5 part	Dipping	1500 hours
8	"	-	Zr 0.5 part Co 5.0 parts	Brushing	1100 hours
9	"	-	Ti 0.5 part	Dipping	660 hours
10	"	-	Mg 0.5 part Mo 0.5 part Sr 0.7 part	Dipping	440 hours
11	"	-	Sn 0.5 part Co 3.0 parts	Dipping	1280 hours
Comp.Ex. No.					
1	Blast coating	CrO ₃ 1.0 part	-	Dipping	800 hours
2	Blast coating	CrO ₃ 2.0 parts Cr(NO ₃) ₃ 2.0 parts	--	Dipping	950 hours
3	Blast coating	CrO ₃ 2.0 parts	-	Dipping	1400 hours
4	Blast coating	-	Tannic acid 1.0 part	Dipping	24 hours
5	Blast coating	-	-	-	10 hours
6	Zinc electro	-	Zr 0.5 part	Dipping	12 hours

Notes to Table 1

1. Blast coating denotes the improved blast zinc coating method.

2. The results of the salt spray test are given in terms of the time (hours) white rust formed.

Claims

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1. A method for treating a metal surface which comprises projecting onto a metal surface a shot-blast particulate material consisting of a core of iron or an iron alloy, an undercoat of an iron-zinc alloy and a top coat of zinc or a zinc alloy, thereby forming a coating film of zinc or the zinc alloy on the metal surface, characterized in that the thus coated metal surface is sequentially brought into contact with
 - an aqueous suspension consisting of 0.1-20 parts by weight of silica per 100 parts by weight of water and
 - an aqueous solution consisting of 100 parts per weight of water and of at least one water soluble metal salt of at least one metal selected among Ti, Zr, Mg, Ba, Sr, W Ni, Co, Sn, Mo and Mn, expressed in terms of 0,01-20 parts by weight of metal ions.
2. A method for treating a metal surface which comprises projecting onto a metal surface a shot-blast particulate material consisting of a core of iron or an iron alloy, an undercoat of an iron-zinc alloy and a top coat of zinc or a zinc alloy, thereby forming a coating film of zinc or the zinc alloy on the metal surface, characterized in that the thus coated metal surface is brought into contact with an aqueous solution consisting of
 - a suspension of 0.1-20 parts by weight of silica per 100 parts by weight of water and
 - at least one water soluble metal salt of at least one metal selected among Ti, Zr, Mg, Ba, Sr, W, Ni, Co, Sn, Mo and Mn, expressed in terms of 0,01-20 parts by weight of metal ions per 100 parts

per weight of water.

Patentansprüche

- 5 1. Verfahren zur Behandlung einer Metallocberfläche, das umfaßt, daß man auf eine Metallocberfläche ein
teilchenförmiges Material zum Strahlen schießt, das aus einem Kern aus Eisen oder einer Eisenlegie-
rung, einer Unterschicht aus einer Eisen-Zink-Legierung und einer Oberschicht aus Zink oder einer
Zinklegierung besteht, wodurch ein Überzugsfilm aus Zink oder der Zinklegierung auf der Metallocberflä-
che gebildet wird, dadurch gekennzeichnet, daß die so beschichtete Metallocberfläche nacheinander in
10 Kontakt gebracht wird mit
 - einer wäßrigen Suspension bestehend aus 0,1 bis 20 Gewichtsteilen Silika pro 100 Gewichtsteilen Wasser und
 - einer wäßrigen Lösung bestehend aus 100 Gewichtsteilen Wasser und mindestens einem
wasserlöslichen Metallsalz von mindestens einem Metall ausgewählt aus Ti, Zr, Mg, Ba, Sr, W,
15 Ni, Co, Sn, Mo und Mn, angegeben als 0,01 - 20 Gewichtsteile der Metallionen.
- 20 2. Verfahren zur Behandlung einer Metallocberfläche, das umfaßt, daß man auf eine Metallocberfläche ein
teilchenförmiges Material schießt, das aus einem Kern aus Eisen oder einer Eisenlegierung, einer
Unterschicht aus einer Eisen-Zink-Legierung und einer Oberschicht aus Zink oder einer Zinklegierung
besteht, wodurch ein Überzugsfilm aus Zink oder der Zinklegierung auf der Metallocberfläche gebildet
wird, dadurch gekennzeichnet, daß die so beschichtete Metallocberfläche in Kontakt gebracht wird mit
einer wäßrigen Lösung bestehend aus
 - einer Suspension aus 0,1 bis 20 Gewichtsteilen Silika pro 100 Gewichtsteilen Wasser und
 - mindestens einem wasserlöslichen Metallsalz aus mindestens einem Metall ausgewählt aus Ti,
25 Zr, Mg, Ba, Sr, W, Ni, Co, Sn, Mo und Mn, angegeben als 0,01 bis 20 Gewichtsteile der
Metallionen pro 100 Gewichtsteile Wasser.

Revendications

- 30 1. Procédé pour le traitement d'une surface métallique qui comprend les opérations consistant à projeter
sur une surface métallique une matière particulière de grenaille constituée par un noyau de fer ou
alliage de fer, une couche inférieure d'alliage fer-zinc et une couche supérieure de zinc ou d'alliage-
zinc, pour former ainsi une pellicule de revêtement de zinc ou d'alliage de zinc à la surface métallique,
caractérisé en ce que la surface métallique ainsi revêtue est séquentiellement mise en contact avec
 35 - une suspension aqueuse constituée par 0,1-20 parties en poids de silice pour 100 parties en
poids d'eau et
 - une solution aqueuse constituée de 100 parties en poids d'eau et d'au moins un sel métallique
hydrosoluble d'au moins un métal choisi parmi Ti, Zr, Mg, Ba, Sr, W, Ni, Co, Sn, Mo et Mn,
exprimé en termes de 0,01-20 parties en poids d'ions métalliques.
- 40 2. Procédé pour le traitement d'une surface métallique qui comprend les opérations consistant à projeter
sur la surface métallique une matière particulière de grenaille constituée par un noyau de fer ou
d'alliage de fer, une couche inférieure d'alliage fer-zinc et une couche supérieure de zinc ou un alliage
de zinc, pour former ainsi une pellicule de revêtement de zinc ou d'alliage de zinc à la surface
métallique, caractérisé en ce que la surface métallique ainsi revêtue est mise en contact avec une
solution aqueuse constituée par
 45 - une suspension 0,1-20 parties en poids de silice pour 100 parties en poids d'eau et
 - d'au moins un sel métallique hydrosoluble d'au moins un métal choisi parmi Ti, Zr, Mg, Ba, Sr,
 W, Ni, Co, Sn, Mo et Mn, exprimé en termes de 0,01-20 parties en poids d'ions métalliques pour
 50 100 parties en poids d'eau.